Framework Assembly Engineering. Effects of Nitro Groups on Assemblies of Phenyldicarboxylates

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A novel 2-D complex [Cu(nbdc)(phen)(H_2O)] (nbdc = 2-nitro-1,4-benzenedicarboxylate dianion and phen = 1,10-phenanthroline) has been synthesized and structurally characterized by single crystal X-ray analysis. It exhibits nice fluorescent property. The modifying group plays a key role in the assembly of the framework.

Design and construction of novel or given frameworks analogous to important minerals such as zeolite, clay, and quartz using phenyldicarboxylates are of much current interest.[1] Recently, much attention has been focused on the use of 1,4-benzenedicarboxylic acid (H_2bdc) while limited researches were devoted to substituted 1,4-benzenedicarboxylic acid (H_2sbdc).[2] Several reports have shown that the framework or functionality could be tuned by pending groups of phenyldicarboxylates because the angle of two carboxylates of 1,4-benzenedicarboxylate is directly related to the size and nature of substituents on the phenyl ring.[3] Moreover, the pending group of phenyldicarboxylates may act as the third coordinate site and further form novel networks. Therefore, H_2sbdc may offer some novel structural and functional interests, for example, the methane adsorption ability of complex $Zn_4O(cbdc)_3$ (cyclobutyl-1,4-benzenedicarboxylic acid, H_2cbdc) is significantly larger than that of $Zn_4O(bdc)_3$ although the latter has larger porosity. The pending group of cyclobutyl of cbdc may tune the framework so that nice methane adsorption could be achieved.[3c] The system of Cu^{2+}/phenanthroline/H_2bdc has been raised much interest due to magnetic and fluorescent properties and at least five species have been synthesized while the frameworks of complexes are only limited in dimer or 1-D networks,[4] in which bdc is a bis-monodentate ligand and shows common coordination topology. Considering the functionality of the pending group of substituent phenyldicarboxylates, we have chosen 2-nitro-1,4-benzenedicarboxylic acid (H_2nbdc) to construct new frameworks. In this paper we report the novel 2-D structure assembled by H_2nbdc with nitro substituent, $\{[Cu(nbdc)(phen)](H_2O)\}_n$ (**1**).

The compound of **1** was synthesized by hydrothermal reaction of copper chloride, 2-nitro-1,4-benzenedicarboxylic acid, and 1,10-phenanthroline in water.[5] The single crystal X-ray analysis revealed that the complex consists of 2-D structure.[6] The copper atom displays square pyramidal geometry, which is completed by two nitrogen atoms from one 1,10-phenanthroline, three carboxylate oxygen atoms from three nbdc ligands (Figure 1). The O(1) is sitting on the apical position (Cu(1)–O(1) = 2.390(3) Å) while O(5), O(1*), N(3), and N(4) occupy the basal plane. There are two kinds of nbdc coordination modes in complex **1**. One mode is bis-monodentate while another is bis-mono-atomic bridge mode.

The bis-mono-atomic bridge mode is extremely sparse.[7]

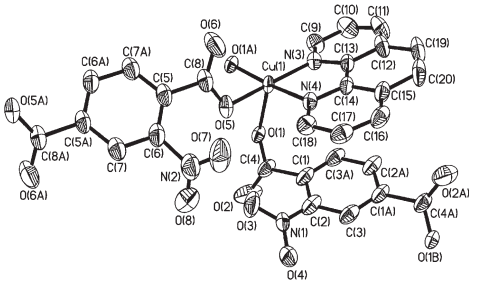

Figure 1. ORTEP view of complex $\{[Cu(nbdc)(phen)](H_2O)\}_n$; selected bond lengths and angles (Å,°):Cu(1)–O(1) 2.390(3), Cu(1)–O(1A) 1.964(2), Cu(1)–O(5) 1.957(3), Cu(1)–N(3) 2.012(3), Cu(1)–N(4) 2.014(3), O(1)–Cu(1)–O(5) 87.46(11), O(1)–Cu(1)–O(1A) 76.58(11), O(1)–Cu(1)–N(3) 98.94(12), O(1)–Cu(1)–N(4) 108.35(11), O(5)–Cu(1)–O(1A) 89.47(12), N(3)–Cu(1)–N(4) 81.85(13).

Each of the two carboxyl groups in μ_4-nbdc offers a mono-atomic bridge by using one oxygen atom as the asymmetric μ-O bridge bound to two copper^{II} ions in apical and basal positions. The oxygen bridging spacers form a four-membered ring, $[Cu_2O_2]$ second building unit (SBU), which is a basic unit, extend the structure into 1-D and 2-D networks (Figure 2). As expected, $[Cu_2(\mu_4\text{-nbdc})]$ units consist of a 1-D chain with SBUs of $[Cu_2O_2]$ and the separation of Cu···Cu in SBU $[Cu_2O_2]$ is 3.428 Å. The separations of Cu···Cu through μ_4-nbdc are 11.073 and 8.729 Å, respectively. The short distance of Cu···Cu separated by nbdc is extremely rare only found in mono-atomic bridge cases and corresponding separations of Cu···Cu in complex Cu_2(*trans*-oxen)(bdc)·$2H_2O$ (**2**) are 10.987 and 9.672 Å,[7] respectively. The bis-monodentate nbdc bridging linkers connect one-dimensional chains of $[Cu_2(\mu_4\text{-nbdc})]$ via four-membered ring units of $[Cu_2O_2]$ into 2-D framework. The separation of Cu···Cu by bis-monodentate nbdc is 10.989 Å. It is obvious

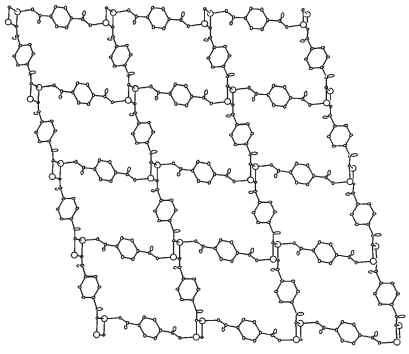

Figure 2. A view of 2-D network constructed by nbdc ligands. The nitro groups are omitted for clarity.

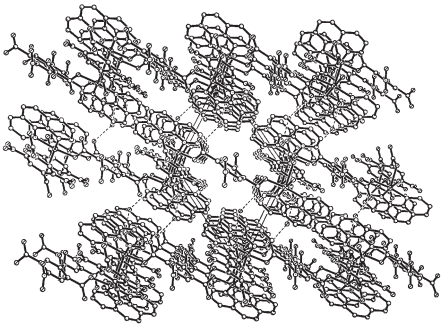

Figure 3. A view of 3-D hydrogen bonding network.

that the 2-D network consists of, in nature, $[Cu_2O_2 + nbdc]_4$ building blocks. The basic unit in 2-D is a grid of $[Cu_4(\mu_4\text{-nbdc})_2(\mu_2\text{-nbdc})_2]$ with dimensions ca. 9.4×11.3 Å. The assembly of the novel 2-D coordination network is attributed to the nitro group through steric and electric effects.

The 2-D network of $[Cu_2(\mu_4\text{-nbdc})(\mu_2\text{-nbdc})]_n$ is created without phenanthroline linking. It seems that the phenanthroline is not necessary in the synthetic viewpoint. However, it could be necessary in the construction of network because the phenanthroline can complete the geometry of the copper atom. The water molecules between the 2-D sheets form hydrogen bonds with the uncoordinating carboxyl oxygen atoms of μ_4-nbdc and μ_2-nbdc from neighboring 2-D layer to hold nets together and build up the 3-D framework (Figure 3).

As mentioned in complexes of [Cu(bdc)(phen)] (**3**)[4c] and Cu_2(*trans*-oxen)(bdc)·$2H_2O$, bis-monodentate bdc ligands lead to a 1-D zig-zag chain structure of **3** and μ_4-bdc ligands creat 1-D chain of **2** although oxen ligands further extend the structure into 2-D framework. Obviously complex **1** combines the characteristics in both **2** and **3** and creates a novel 2-D framework, which is attributed to the effect of nitro group. The successful syntheses of complexes **1** and **2** suggest that 2-D structure for complex [Cu(bdc)(phen)] could be achieved at suitable micro synthetic environment (equivalent to the effect of nitro group, such as in **2**) although many efforts have been done.

The UV–vis spectrum of **1** exhibits three high-energy absorptions at 191, 222, and 299 nm in the solid state; the latter can be assigned to ligand-to-metal charge transfer. An intense fluorescent emission of **1** at 453 nm ($\lambda_{ex} = 230$ nm) was observed in the solid state at room temperature and is assigned to the ligand-to-metal charge transfer band and some σ-donations from the cooperation of 1,10-phenanthroline and nbdc ligands. This information suggests that **1** might be an excellent candidate for potential photoactive material.

In summary, we have successfully synthesized a novel 2-D compound [Cu(nbdc)(phen)](H_2O) constructed from 2-nitro-1,4-benzendicarboxylic acid and 1,10-phenanthroline with nice fluorescent property. Combination of μ_4-nbdc and μ_2-nbdc leads to new assembly of benzenedicarboxylates, which may be of great benefit for designing and controlling the frameworks constructed from benzenedicarboxylates.

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References and Notes

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5 Prepartion of compound **1**. A mixture of $CuCl_2·2H_2O$ (0.0352 g, 0.2 mmol), 2-nitro-1,4-benzenedicarboxylic acid (H_2nbdc, 0.0452 g, 0.2 mmol), 1,10-phenanthroline (0.0301 g, 0.15 mmol) and H_2O (8 mL) in the molar ratio ca. 1:1:0.74:2151 was sealed in a 25 mL stainless-steel reactor with Teflon liner and was heated at 150 °C for 3 h. After cooling, deep blue crystals of **1** were collected by filtration. Yield: 87%. Anal. calcd. for $C_{20}H_{13}CuN_3O_7$: C, 51.02; H, 2.78; N, 8.92%; found: C, 51.22; H, 2.56; N, 8.84%. IR (KBr, cm^{-1}): 1638 (s), 1609 (s), 1522 (m), 1489 (m), 1431 (m), 1364 (s), 1341 (s), 1250 (m), 1151 (w), 854 (m), 722 (m), 649 (w), 513 (w). Thermogravimetric analysis of **1** shows that in the range 100 to 180 °C, weight loss is 4.1% (calcd: 3.8%), which corresponds to the loss of one water molecule. The residue is CuO at 655 °C (found: 15.2%, calcd: 16.9%).

6 X-ray crystal structure determination of **1**: A deep blue crystal having the size of $0.24 \times 0.32 \times 0.55$ mm was mounted on a glass fiber and data collection was done on a Bruker SMART CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods and successive Fourier syntheses using SHELXS-97. The structure was refined by full-matrix least-squares techniques using SHELXL-97. Crystal data for **1**: $C_{20}H_{13}CuN_3O_7$, M = 470.87, triclinic, $P\bar{1}$, $a = 9.3623(4)$, $b = 10.7706(5)$, $c = 11.2802(5)$ Å, $\alpha = 61.691(2)$, $\beta = 88.440(2)$, $\gamma = 70.695(2)°$, $V = 933.56(7)$ Å^3, $Z = 2$, $D_c = 1.675$ g·cm^{-3}, $\mu = 1.222$ mm^{-1}, $R_1 = 0.0537$ and $wR_2 = 0.1507$. CCDC number is 211902.

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